

**NASA
Technical
Paper
2611**

July 1986

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National Aeronautics
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Scientific and Technical
Information Branch

Summary

The oxidation characteristics of a pure ester (trimethylpropane triheptanoate) were studied by using a chemiluminescence technique. Tests were run in a thin-film microoxidation apparatus with an aluminum-alloy catalyst. Conditions included a pure-oxygen atmosphere and a temperature range of 176 to 206 °C. Results indicated that oxidation of the ester (containing 10^{-3} M diphenylanthracene as an intensifier) was accompanied by emission of light. The maximum intensity of light emission I_{\max} was a function of the amount of ester, the concentration of intensifier, and the test temperature. The induction period, or the time to reach one-half of maximum intensity $t_{1/2}$, was inversely proportional to test temperature. Decreases in light emission at the later stages of a test were caused by depletion of the intensifier.

Introduction

Advanced aircraft will place increased thermal stresses on lubricants and hydraulic fluids. Maximum fluid temperatures in excess of 316 °C have been forecast for future applications (refs. 1 to 3). The primary limitation at these temperatures is normally oxidation, which results in fluid degradation, viscosity increases, and the production of sludge and deposits (refs. 4 and 5). Over the years many tests have been devised to simulate the oxidizing environment, which includes the effect of catalytic materials (ref. 5). Recently a sensitive microoxidation test has been developed at Pennsylvania State University (ref. 6) that effectively simulates the conditions (thin lubricant film on a hot metal surface) in a lubricating environment (refs. 4 and 7).

One phenomenon associated with lubricant oxidation is chemiluminescence, or visible light emission during the oxidation process (ref. 8). Although this light emission is very weak, it can be measured accurately with modern highly sensitive detectors. Advantages of using emitted light as a means of studying oxidation include the following (refs. 9 and 10):

- (1) It is very sensitive.
- (2) It is noninvasive.
- (3) The reaction can be followed as a function of time.
- (4) Certain kinetic parameters can be extracted from the light emission data.

A comprehensive review of the use of chemiluminescence for fuel and lubricant oxidation studies appears in reference 11. A brief discussion of oxidation and chemiluminescence appears in the next section.

Background

Chemiluminescence (CL), the light emitted as a result of a chemical reaction, has been recognized since antiquity. It occurs when a chemical reaction produces a molecule that is in an excited electronic state. As this molecule relaxes to ground state, a photon is emitted, and light is observed in the visible range. A highly efficient CL process occurs naturally in the biological systems of fireflies and some marine organisms (ref. 12).

Electrochemically generated CL, peroxide reactions, and oxidation of hydrocarbons are typical low-efficiency processes requiring more sensitive equipment than the human eye for detection and study. This work concerns, in particular, CL that results from autoxidation, or oxidation with molecular oxygen, of organic lubricants.

Reaction Mechanism

Initiation

Autoxidation of an organic compound usually proceeds by a free-radical chain mechanism. A simplified mechanism is thought to occur as follows (ref. 13):



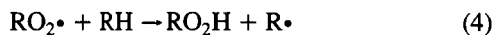
Here an initiator Int produces free radicals $\text{Int}\cdot$ at reaction rate R_i . The free radical then abstracts a proton from the hydrocarbon RH to produce an alkyl radical $\text{R}\cdot$.

Propagation

The alkyl radical $\text{R}\cdot$ reacts with molecular oxygen O_2 in the propagation step of the chain reaction:



This step produces a peroxy radical $RO_2\cdot$ which, in turn, reacts with the parent hydrocarbon RH to produce a hydroperoxide RO_2H :



This reaction regenerates the original free radical $R\cdot$, which propagates the chain.

Termination

The chain reaction can be terminated by radical coupling of two peroxy radicals $RO_2\cdot$



by cross termination of the alkyl radical $R\cdot$ and a peroxy radical $RO_2\cdot$



or by reaction of two radicals $R\cdot$



Normally, when oxygen is present, the concentration of peroxy radicals is much greater than the concentration of alkyl radicals ($[RO_2\cdot] \gg [R\cdot]$), and reactions (6) and (7) can be disregarded. The actual termination reaction is then reaction (5).

Chemiluminescence

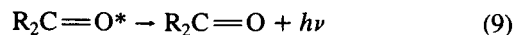
Excited States

In reaction (5), the product RO_4R is a tetroxide which will further decompose to form a ketone $R_2C=O$, an alcohol R_2CHOH , and molecular oxygen O_2 :

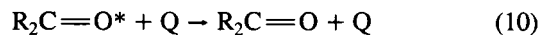


(equation not balanced)

It is believed that CL originates from reaction (8) (ref. 9). A very small number of the ketone molecules $R_2C=O$ produced in this reaction are in an excited singlet or triplet state $R_2C=O^*$. Perhaps one photon is emitted for every 10^8 to 10^{10} terminations.



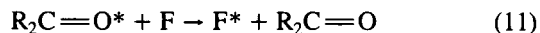
This inefficiency is, in part, due to quenching of the excited ketone by oxygen or other species Q :



The intensity of the emitted radiation $h\nu$ is directly proportional to the square of the peroxy radical concentration $[RO_2\cdot]^2$. This dependence is the basis for determining the concentration of peroxy radicals and thus the kinetics of hydrocarbon oxidation.

Intensifiers

The intensity of light emission can be greatly enhanced by the addition of small quantities of chemically inert materials which have high fluorescent efficiencies (ref. 10). These "fluors" F increase the intensity by energy transfer from the excited ketone to the fluorescent additive:



This may increase the CL sensitivity by several orders of magnitude.

Emission as Function of Time

An idealized curve of light emission as a function of time for an oxidation reaction is shown in figure 1. The emission of light gradually increases as oxidation proceeds, and the concentration of peroxy radicals increases until steady state is reached. At this point the light intensity reaches a maximum I_{\max} . The time to reach this maximum t_{\max} is a measure of the induction period. More commonly, the time to reach one-half of maximum intensity $t_{1/2}$ is used.

If the oxygen flow is shut off while the oxidation reaction is proceeding, there is sometimes an immediate increase in light emission. This occurs because O_2 molecules are effective quenchers for the excited state species (ref. 11). The

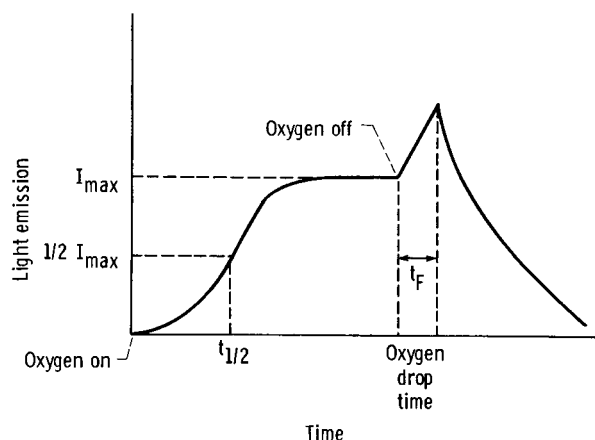


Figure 1.—Idealized curve of light emission as function of time for oxidation reaction.

time between oxygen cutoff and the eventual drop in light emission is called the oxygen drop time t_F .

The oxygen drop time is a direct measure of oxygen consumption and, therefore, a direct measure of the reaction rate. The oxygen concentration in the oil film at the oxygen cutoff point must be known so that oxygen consumption can be calculated.

Apparatus

Microoxidation Apparatus

Figure 2 illustrates the microoxidation apparatus used in this study. It is a modification of the oxidation apparatus developed at Pennsylvania State University (refs. 6 and 7). It consists of two heat-resistant glass sections connected by a ground glass joint. The catalyst specimen is held in place by an annular glass ring on the base of the outer, or lower, section. The material to be oxidized is placed on the catalyst surface. The fiber-optic probe used to sense the light emission from the catalyst surface is held in the inner, or upper, section. This assembly consists of two vertical, concentric tubes forming an annular space for reduction of heat transfer to the probe, which contains a heat-sensitive epoxy. The bottom of each of these tubes is sealed with a quartz window to prevent absorption of the emitted light before it can be detected. The upper section also contains a gas inlet tube for oxygen or argon flow. The distance from the end of the fiber-optic probe to the top of the ester film is approximately 1.5 cm.

Chemiluminescence Apparatus

A schematic diagram of the chemiluminescence apparatus is shown in figure 3. The system consists of the fiber-optic probe, a photomultiplier tube (PMT) and housing, an amplifier/discriminator, a high-voltage power supply, a rate meter, and a recorder.

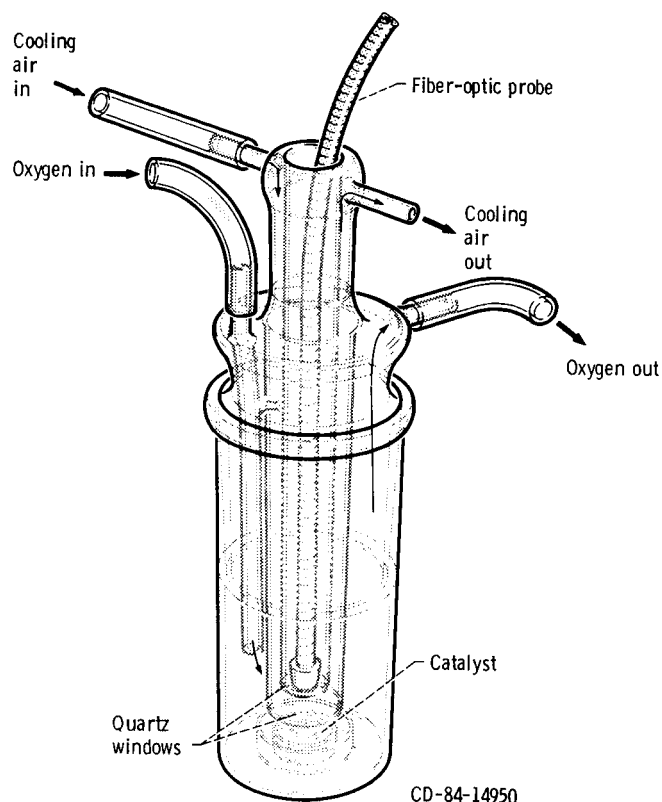


Figure 2.—Microoxidation apparatus.

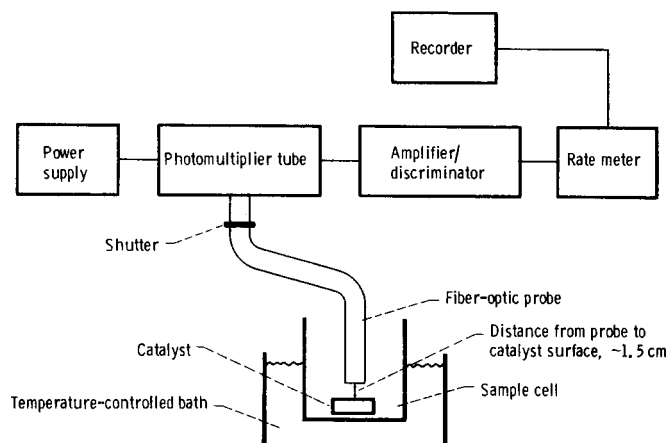


Figure 3.—Schematic of chemiluminescence apparatus.

The fiber-optic probe is a bundle of quartz fibers (50 cm long) covered with a flexible stainless steel sheath (~7 mm o.d.). One end of the probe is inserted into the microoxidation apparatus; the other end is attached to a flange on the PMT housing. The flange contains a manually operated shutter. The photomultiplier tube has a dark current of 4 nA and a spectral response range of 160 to 850 nm. The housing also contains a thermoelectric refrigerated chamber in order to cool the photomultiplier-tube cathode to approximately 40 °C below ambient.

The input pulse from the PMT is fed into an amplifier/discriminator mounted inside the PMT housing. The output from the amplifier/discriminator is connected to a rate meter, which measures the rate of input pulses. (A 30-sec time constant was used in these studies.) The count rate is displayed on a panel meter. There is also an analog voltage output to power a strip-chart recorder.

Bath and Lighttight Enclosure

A high-temperature (250 °C), constant-temperature bath was used in these studies. A high-viscosity silicone fluid served as the heat transfer medium. Bath specifications indicated temperature control to ± 0.1 °C, but, due to the high silicone viscosity, temperature variations of ± 1 °C were common.

A cylindrical aluminum sleeve is mounted in the bath opening (10 cm long, 5 cm i.d., and 6.5 cm o.d.) with approximately 7 cm submerged in the bath fluid. A platinum resistance thermocouple is mounted vertically in the side of the sleeve to a depth of 9 cm. This couple is connected to a digital readout (accurate to ± 0.1 °C), which has a minimum/maximum recall mode to determine the temperature range during an experiment.

The bath and PMT housing are located inside a lighttight metal box located in the corner of a fume hood. A handle on the top of the box is used to operate the PMT shutter remotely.

Procedure

At least 2 hr before a test, the PMT system was turned on and allowed to stabilize. The thermoelectric cooling system was maintained continuously. The supply voltage to the PMT was kept constant at a setting of 1000 V.

The microoxidation apparatus was thoroughly cleaned with trichlorotrifluoroethane and allowed to air-dry. The catalyst was cleaned with trichlorotrifluoroethane, scrubbed with a paste of submicron alumina, and rinsed with tap water and then distilled water. After air-drying, the catalyst was weighed and placed with forceps into the bottom of the lower section of the microoxidation apparatus. Next the catalyst and the lower section of the apparatus were weighed together. Then six drops of ester were placed on the catalyst surface by pipette, and the section was reweighed to determine the exact amount of added ester.

The upper apparatus section was inserted into the lower section, and the device was purged with argon for 5 min at room temperature (flow rate > 75 ml/min). Next the assembled apparatus was placed in a steel holder on a hot plate previously heated to 130 °C and purged with argon at this temperature for 20 to 25 min to remove dissolved oxygen and water from the ester film.

At this point the apparatus was placed in the aluminum block in the bath, which had previously been heated to test temperature. The fiber-optic probe was inserted in the upper section of the apparatus, and a high flow rate of air was

directed into the annular region around the fiber-optic probe for cooling. The top of the apparatus was covered with aluminum foil to block any stray light, and the front cover of the enclosure was put in place.

While the apparatus was being purged initially, a baseline count rate with the PMT shutter closed was determined. After the lighttight box was closed, the PMT shutter was opened, and a new baseline was measured during temperature equilibration. After 20 to 30 min the argon flow was turned off, and simultaneously the oxygen flow was begun. The intensity of emitted light was recorded continuously on a strip-chart recorder. After the light intensity reached a maximum, the test was continued for another 5 to 15 min, and then the oxygen and argon flows were exchanged.

The box was opened, and the apparatus still under an argon purge was removed and allowed to cool. The two sections were separated, and the lower part was weighed to determine the ester weight loss. Then 4 ml of chloroform was added to the lower section to dissolve the remaining ester. This sample was retained for high-pressure liquid chromatographic analysis (HPLC). The catalyst was thoroughly rinsed with trichlorotrifluoroethane, allowed to air-dry, and weighed to determine whether deposits remained on the catalyst.

Materials

Lubricant

An ester (trimethylpropane triheptanoate, TMPH) was used in these studies. Its structure is shown in figure 4(a), and some of its chemical and physical properties are given in table I.

Intensifier

To increase the efficiency of light emission, 9,10-diphenylanthracene (DPA) (99-percent pure) was used as an intensifier. Its structure is shown in figure 4(b).

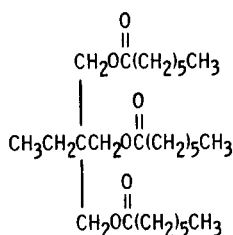
Catalyst

The catalyst material used was aluminum alloy 2024, which has the following nominal composition: 3.8 to 4.9 percent copper, 0.3 to 0.9 percent manganese, 1.2 to 1.8 percent magnesium, balance aluminum. This alloy was chosen because it is the aluminum alloy used in the standard oxidation-corrosion test developed by the Air Force (ref. 14). The dimensions of the catalyst are illustrated in figure 5.

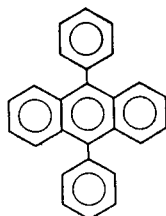
Results

Maximum Light Emission as Function of Time

Light emission data as a function of time are shown in figure 6 for various temperatures. Maximum light emission increases with increasing temperature. The curves have been offset for clarity. The general form of the emission curve is



(a)



(b)

- (a) Trimethylolpropane triheptanoate.
 (b) 9,10-Diphenylanthracene.

Figure 4.—Chemical structures.

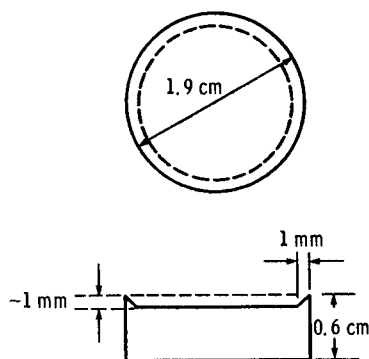


Figure 5.—Catalyst dimensions.

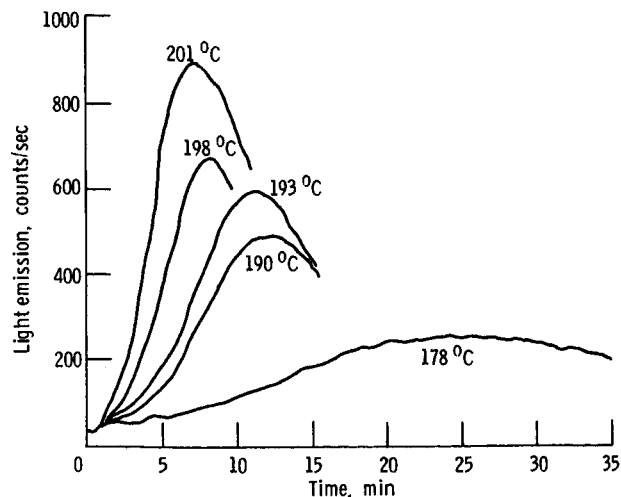


Figure 6.—Light emission as function of time for TMPTH with 10^{-3} M DPA at various temperatures. Aluminum-2024 catalyst; oxygen atmosphere.

a buildup to I_{\max} and then a gradual dropoff. The higher the temperature, the more rapid the dropoff of light emission. The maximum light emission I_{\max} and the time for the emission to reach one-half of I_{\max} are determined from these curves. These data are summarized in table II.

Maximum Light Emission as Function of Sample Size

A few tests were run at nearly constant temperature (178.3 to 179.5 °C) with different sample sizes. Maximum light emission I_{\max} as a function of sample size appears in figure 7. An essentially linear relationship between I_{\max} and sample size was observed. It became apparent that in order to correlate the I_{\max} data some form of normalization was necessary. Even using the same number of drops of lubricant yielded slightly different weights. Therefore, a normalized maximum emission I_{\max}^* was calculated by dividing the observed I_{\max} by a normalized weight. This weight was calculated by dividing the lubricant sample size from each test by 0.0512, which was the minimum sample size in this test series (from test B-36). These normalized weights and the calculated I_{\max}^* are also summarized in table II.

I_{\max}^* as Function of Temperature

Normalized maximum light emission I_{\max}^* as a function of temperature appears in figure 8. The data are fitted with a geometric-least-squares equation.

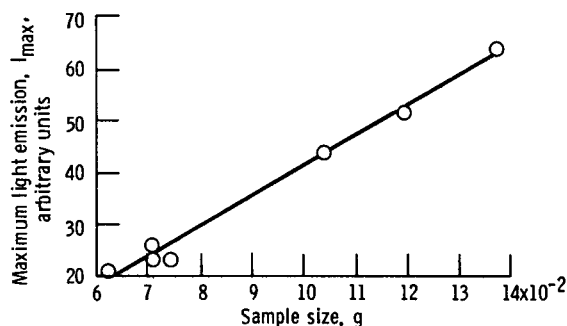


Figure 7.—Maximum light emission as function of sample size. Temperature, 178.3 to 179.5 °C; DPA (10^{-3} M) in TMPTH; aluminum-2024 catalyst; oxygen atmosphere.

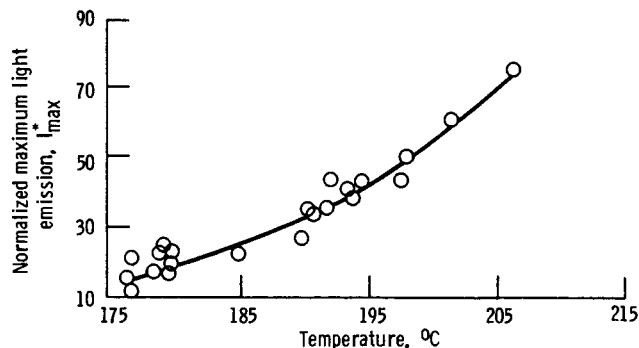


Figure 8.—Normalized maximum light emission as function of temperature. DPA (10^{-3} M) in TMPTH; aluminum-2024 catalyst; oxygen atmosphere.

Log I_{\max}^* as Function of $1/T$

The data from figure 8 are replotted in Arrhenius fashion in figure 9. Here the log of the normalized maximum light emission is plotted as a function of the reciprocal of the absolute temperature by using a linear-least-squares fit. A correlation coefficient of 0.951 was obtained.

Log($t_{1/2}$)⁻¹ as Function of $1/T$

Another Arrhenius plot appears in figure 10. Here the log of the reciprocal of the time to reach one-half maximum light emission ($t_{1/2}$)⁻¹ is plotted as a function of the reciprocal of absolute temperature. A correlation coefficient of 0.962 was determined.

Discussion

Chemiluminescence as Function of Time

As expected, very low background levels of light emission (50 to 100 counts/sec) were obtained while the apparatus was being purged with argon. After the oxygen flow was initiated, there was no change in light intensity for approximately 45 sec. Then light emission increased for approximately 30 sec.

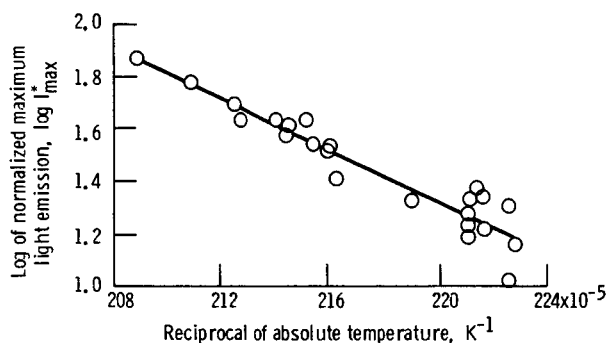


Figure 9.—Log of normalized maximum light emission as function of reciprocal of absolute temperature. DPA (10^{-3} M) in TMPTH; aluminum-2024 catalyst; oxygen atmosphere.

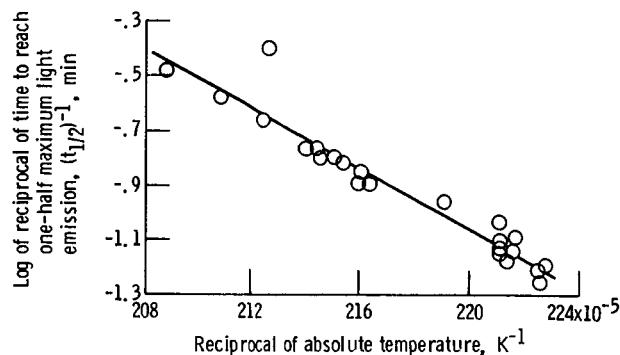


Figure 10.—Log of reciprocal of time to reach one-half maximum light emission as function of reciprocal of absolute temperature.

The rate of increase decreased at this point but still continued to build up to a maximum.

The initial delay is most likely due to the time required for the argon to be swept out of the chamber by the oxygen and for the subsequent diffusion of oxygen into the lubricant film.

The initial increase in light emission, which produces a small shoulder on the emission curve, may be due to the presence of adventitious peroxides or other species which may cause enhanced chemiluminescence. Similar behavior has been reported in oxyluminescence studies of polymers (ref. 15).

One would now expect a buildup to steady state and a maximum level of light emission, as indicated in the idealized curve of figure 1. However, the maximum emission is sustained only for a short time. There is a dropoff in intensity which is more pronounced as test temperature increases.

This could be caused by one of several factors:

(1) The oxidation rate decreased because of high conversion of the starting material (ester).

(2) The oxidation rate decreased because of the formation of natural inhibitors.

(3) The oxidation rate was constant, but the quantum efficiency of the light-emission reaction decreased because of increased quenching of the excited state by some product formed during the oxidation process.

(4) The oxidation rate was constant, but the intensifier DPA was depleted.

One drawback of the microoxidation apparatus is that at high temperatures much of the material is degraded (sometimes more than 50 percent) (ref. 5). However, because of the sensitivity of the CL method, tests can be run at much lower temperatures (generally less than 200 °C), where conversion may be only a few percent.

HPLC analysis of the oxidized lubricant as a function of test time indicated that the oxidation rate was not decreasing and that much starting material remained. Therefore possibilities (1) and (2) can be excluded.

There is no easy way to determine whether possibility (3) occurred. However, HPLC analysis of the oxidized lubricant indicated a continual decrease in DPA concentration as a function of test time (fig. 11). Size-exclusion chromatography showed almost a complete loss of DPA after 30 min at 190 to 193 °C. The same analysis showed a continued increase in high-molecular-weight products of the oxidized ester.

Several tests were then performed by using different molar concentrations of DPA (0.5×10^{-3} , 2×10^{-3} , and the standard 1×10^{-3}) at 191 to 192 °C. The amount of test lubricant was nearly constant for each test. Figure 12 is a plot of I_{\max} (not normalized) as a function of molar concentration of DPA. It is apparent that a linear relation exists between I_{\max} and the amount of DPA.

Intensifier Depletion

The CL literature does not address the problem of intensifier depletion. All reported work has been done on bulk solutions for which intensifier depletion is apparently not significant.

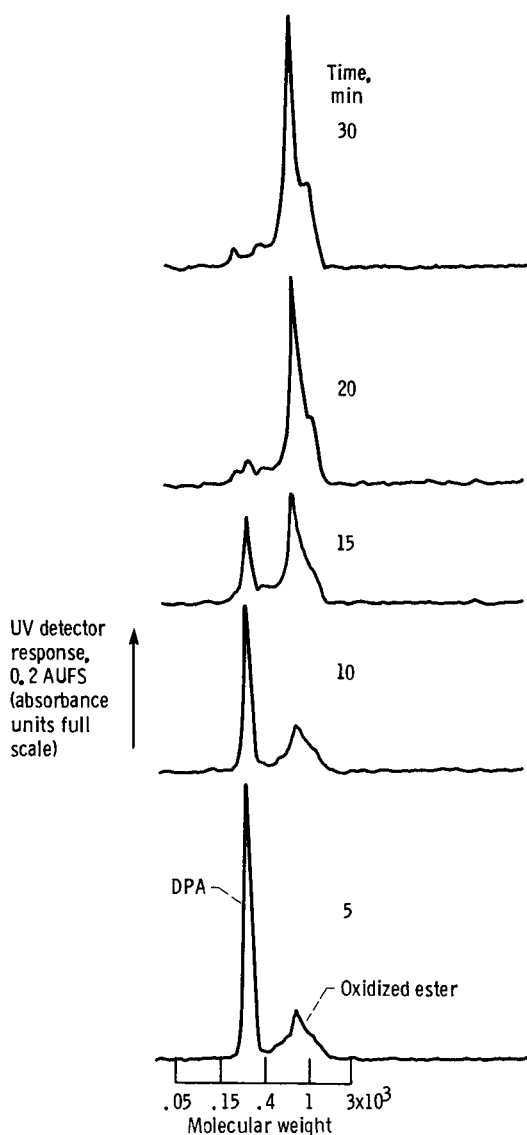


Figure 11.—Size-exclusion chromatograms of oxidized TMPTH with 10^{-3} M DPA at various test times. Temperature, 190 to 193 °C; aluminum-2024 catalyst; oxygen atmosphere.

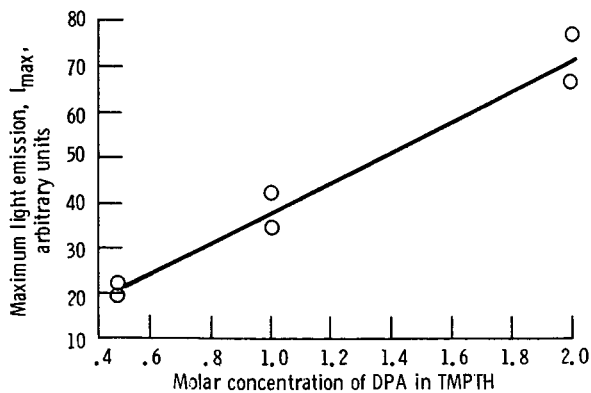


Figure 12.—Maximum light emission as function of molar concentration of DPA in TMPTH. Temperature, 191 to 192 °C; aluminum-2024 catalyst; oxygen atmosphere.

Lundeen and Livingston did report a linear dependence of intensity on intensifier concentration (ref. 16). From their tests they also reported that CL intensity rose to a maximum and then slowly decreased. However, they gave no reason for this phenomenon.

Depletion of additives from thin films was reported by Sniegowski (ref. 17). He showed that two commonly used antioxidants were rapidly depleted from thin oil films placed on bearing steels and exposed to air at room temperature. Therefore, it may not be surprising that DPA was depleted at elevated temperatures. However, the loss of DPA was not solely due to evaporation. A test run in argon (B-47) at 194 °C showed little depletion of DPA. Therefore, depletion is definitely related to the oxidation process.

The exact fate of the DPA is not known. It is either oxidized to a more volatile component or adsorbed on the catalyst specimen. Tests conducted with rubrene, a higher-molecular-weight intensifier, produced similar results.

It is possible to run tests without added intensifier. However, when that was tried (test B-37), light emission was very low (approximately an order of magnitude less than tests with 10^{-3} M DPA) at a test temperature of 179 °C.

It should be noted that an intensifier has a function other than increasing the efficiency of the emission process. When hydrocarbons oxidize, they often form fluorescent products, which can then affect the light emission in an unpredictable manner. The addition of an intensifier effectively masks this problem.

Since there is a linear dependence of light emission on intensifier concentration, CL emission curves can be corrected if the actual intensifier concentration is known. For example, taking data from the size-exclusion curves of figure 11, one can construct a curve for DPA concentration as a function of time in the temperature range 190 to 193 °C. These data appear in figure 13 and are represented with an exponential-least-squares fit.

The actual light emission as a function of time for test B-53 (temperature, 191.9 °C) appears in figure 14. When the data from figure 13 are used, and a linear dependence of emission on DPA concentration is assumed, an adjusted emission curve is obtained. This curve represents the actual light emission

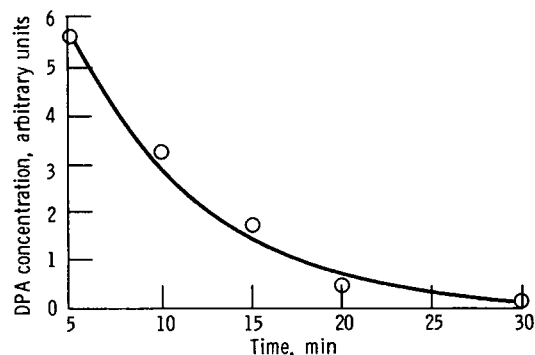


Figure 13.—Concentration of DPA as function of test time. Temperature, 190 to 193 °C; aluminum-2024 catalyst; oxygen atmosphere.

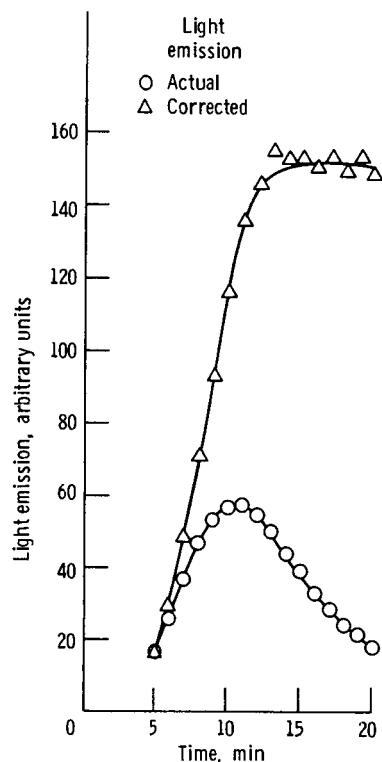


Figure 14.—Actual light emission for test B-53 and emission corrected for DPA depletion as functions of time. Temperature, 191.9 °C; aluminum-2024 catalyst; oxygen atmosphere.

as a function of time without regard to intensifier depletion. The adjusted curve corrected for DPA depletion shows a plateau, which is the expected feature at steady state.

There are two other important points to be drawn from this corrected curve. First, the maximum light emission I_{\max} is much larger than the experimentally obtained data. Obviously, this difference depends on temperature, and it is more pronounced at higher temperatures. In addition, the time to reach the plateau on the corrected curve and I_{\max} for the actual emission curve are different. Therefore $t_{1/2}$ is different. These factors are considered in the section Activation Energy.

Chemiluminescence From Intensifier

The intensifier itself may chemiluminesce under the conditions of these experiments. Neat DPA was placed on an aluminum catalyst and tested in oxygen at 188 °C (test B-62). The DPA did chemiluminesce under these conditions. However, based on the amount of DPA in this study, its contribution to CL was not significant.

Activation Energy

Some kinetic parameters such as activation energies can be determined from CL data. It has long been recognized that kinetic data over a wide temperature range can be represented by an empirical equation proposed by Arrhenius (ref. 18):

$$k = se^{-E_a/RT} \quad (13)$$

where

k rate constant
 s preexponential factor
 E_a activation energy
 R gas constant
 T absolute temperature

In logarithmic form

$$\log k = \frac{-E_a}{2.303 RT} + \log s \quad (14)$$

Therefore, a straight line should be obtained when $\log k$ is plotted as a function of the reciprocal of the absolute temperature.

It has been shown that k is proportional to I_{\max} , $(t_{1/2})^{-1}$, and t_F^{-1} (ref. 10). The activation energy calculated from the slope of $\log I_{\max}$ as a function of T^{-1} is usually related to the propagation reaction (eq. (4)). When oxygen diffusion into the oil film is rate limiting, $E_{I_{\max}} = E_{\text{propagation}}$ where $E_{I_{\max}}$ and $E_{\text{propagation}}$ are activation energies (ref. 9). The value of $E_{I_{\max}}$ is 9.2×10^4 J/mol (22 kcal/mol) (from fig. 9). Therefore, $E_{\text{propagation}}$ is approximately 4.6×10^4 J/mol (11 kcal/mol). This activation energy based on $(t_{1/2})^{-1}$ is related to the initiation reaction. For auto-oxidation reactions, in the absence of added initiators, the major source of free radicals is probably thermal decomposition of hydroperoxide (ref. 13):



This treatment of I_{\max} and $t_{1/2}$ data yielded reasonable values for activation energies. However, in light of the discussion involving intensifier depletion, it is obvious that both values would be changed considerably if intensifier concentration were constant.

Oxygen-Drop Experiments

As discussed earlier, t_F , or the time for intensity to drop off after the oxygen flow is cut off, can be related to the oxidation rate itself. However, a rise in light intensity after oxygen cutoff was not observed in these studies. Since very little oxygen is contained in the thin film, it may be depleted before any decrease in quenching can be detected. It has also been reported that, when an intensifier is used, the lifetime of the emitting species is sometimes shortened to such an extent that oxygen drop is not observed (ref. 19). The long time constant (30 sec) used in gathering these data also reduces the probability of detection.

Chemiluminescence as Function of Ester Sample Size

Chemiluminescence is a function of the concentration of DPA in TMPTH. It has been reported that CL intensity increases with increasing concentration, or sample size, of test material at low concentrations (ref. 20). A series of tests was performed with neat TMPTH (no intensifier) at approximately 187 °C. These tests (B-63, B-65, B-66, and B-67) are summarized in table II. Figure 15 shows I_{\max} as a function of sample size. At these low sample amounts, CL intensity (I_{\max}) is indeed a linear function of sample size.

Initiators

All tests except B-38 were run without added initiators. In B-38, 10^{-2} M azoisobutyronitrile (AIBN) was added. An induction period of 10.8 min was obtained for this test compared with 15.0 min for test B-35 run at a comparable temperature without an initiator. Although this variation is not much greater than test-to-test reproducibility, future work should employ an initiator to improve induction-period reproducibility.

Chemiluminescence as Function of Wavelength

The PMT used in this study senses radiation in the wavelength range 160 to 850 nm. As indicated in reference 20, the CL spectra will vary depending on what species is actually emitting light. One can obtain some information about the wavelength range for maximum emission by using a series of bandpass filters. Four filters were used in this study, and their characteristics are shown in table III.

Series of identical tests were run with neat TMPTH and TMPTH with 10^{-3} M DPA. Tests were conducted at 187.1 to 187.3 °C with an aluminum-2024 catalyst in an oxygen atmosphere. Tests were performed with no filter and with the various filters attached at the base of the lower quartz window between the sample and the fiber-optic probe. Each test was rerun with a new sample with about the same amount of TMPTH. Normalizing the maximum light emission for each test yielded I_{\max}^* . These data appear in figure 16 for each of

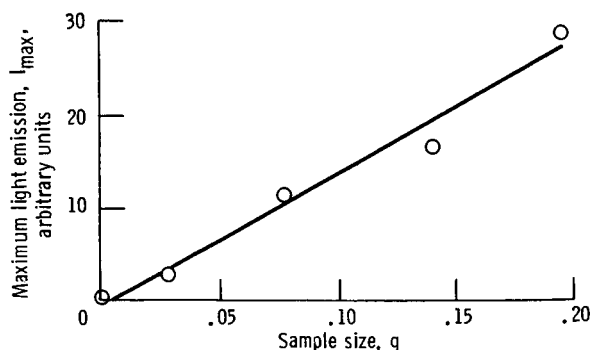


Figure 15.—Maximum light emission as function of sample size for neat TMPTH. Temperature, 187.0 to 187.5 °C; aluminum-2024 catalyst; oxygen atmosphere.

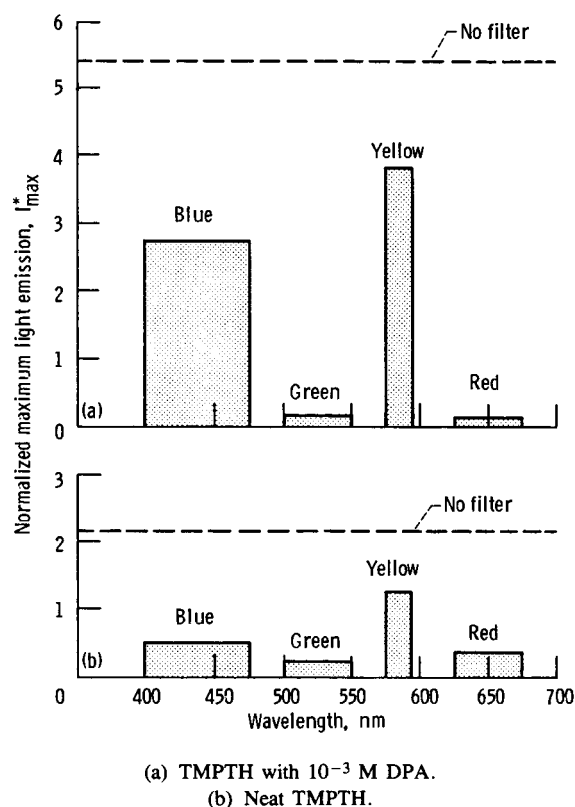


Figure 16.—Normalized maximum light emission for TMPTH with and without DPA (10^{-3} M) for various wavelength regions. Temperature, 187 °C, aluminum-2024 catalyst; oxygen atmosphere.

the various wavelength regions and are summarized in table IV.

With no filter I_{\max}^* was about 2-1/2 times greater for TMPTH with 10^{-3} M DPA than for neat TMPTH. This is contrasted with test B-37 (179.1 °C) which yielded an I_{\max}^* about one ninth of the TMPTH with DPA tests at the same temperature.

With neat TMPTH, the maximum CL appeared in the yellow wavelength region (575 to 595 nm). Another peak appeared in the blue region (400 to 475 nm) for the tests with added intensifier (DPA). This agrees qualitatively with the data of Belyakov and Vassil'ev (ref. 20).

It can be concluded that chemiluminescence is a viable technique for studying oxidation phenomena in thin films. However, problems of intensifier depletion and poor temperature control must be addressed.

Summary of Results

A chemiluminescence technique was used to study the oxidation characteristics of a pure ester (trimethylpropane triheptanoate). Tests were conducted in a thin-film microoxidation apparatus with an oxygen atmosphere over a temperature range of 176 to 206 °C. The following results were obtained:

1. The oxidation of the ester was accompanied by emission of light in the wavelength range 160 to 850 nm.
2. Maximum light emission was a function of the amount of ester, concentration of intensifier, and temperature.
3. Log of the induction period (the time to reach one-half maximum intensity) was inversely proportional to temperature.

4. Decreases in light emission at the later stages of a test were caused by depletion of intensifier.

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National Aeronautics and Space Administration
Cleveland, Ohio, April 5, 1986

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TABLE I.—PHYSICAL AND CHEMICAL PROPERTIES
OF TRIMETHYOLPROPANE TRIHEPTANOATE

Viscosity, cm ² /sec(cSt)	
At 99 °C	3.5 × 10 ² (3.5)
At 38 °C	15.2 × 10 ² (15.2)
At -18 °C	287 × 10 ² (287)
At -40 °C	2400 × 10 ² (2400)
Pour point, °C	-68
Specific gravity at 25 °C	0.963
Color, ASTM	1.0
Flash point, °C	238
Fire point, °C	216
Autoignition temperature, ASTM D2155, °C	463
Moisture content, percent	0.02
Foaming tendency, ASTM D892	
Sequence I	Nil
Sequence II	Nil
Sequence III	Nil
Evaporation, wt%	
After 6.5 hr at 204 °C	6.0
After 22 hr at 149 °C	0.38
Shell four-ball wear test	
Scar diameter, at 54 °C and 600 rpm for 1 hr, mm	
1-kg load	0.21
10-kg load	0.43
40-kg load	0.57

TABLE II.—SUMMARY OF TEST DATA

[Lubricant, trimethylpropane triheptanoate; catalyst, aluminum alloy 2024; atmosphere, oxygen; intensifier, 9,10-diphenylanthracene (10^{-3} M).]

Test	Lubricant weight, g	Normalized weight	Maximum light emission, I_{\max} , arbitrary units	Normalized maximum light emission, I_{\max}^*	Induction time, $t_{1/2}$, min	Average temperature, °C	Total test time, min
B-23	0.0671	1.31	19	14.5	15.5	176	40
B-24	.0701	1.37	14.5	10.6	18.0	176.5	43
B-29	.1211	2.37	49	20.7	15.8	176.5	60
B-32	.0702	1.49	23	16.8	12.3	178.3	36
B-30	.1189	2.32	51.5	22.2	14.0	178.5	35
^a B-38	.0699	1.37	26	19	10.8	178.8	33
B-35	.1367	2.67	64	24	15.0	178.9	45
^b B-37	.0686	1.34	3	2.2	6.5	179.1	30
B-25	.0742	1.45	23	15.9	13.8	179.5	36
B-26	.0707	1.38	26	18.8	13.5	179.5	33
B-27	.0620	1.21	21	17.4	10.8	179.5	60
B-28	.1036	2.02	44	21.8	12.5	179.5	60
B-36	.0512	1.00	21.5	21.5	9.3	184.6	30
^b B-63	.0773	1.51	11.5	7.6	2.7	187.0	30
^b B-65	.1395	2.72	16.5	6.1	3.3	187.3	30
^b B-66	.0278	.543	3.0	5.5	3.3	187.4	30
^b B-67	.1942	3.79	29.0	7.7	2.1	187.5	30
^f B-62	.0458	----	11.0	----	---	188.0	30
B-39	.0717	1.40	36.5	26.1	7.8	189.6	20
B-48	.0692	1.35	46.5	34.4	7.0	190	15
B-40	.0696	1.36	46	33.8	7.8	190.2	20
B-51	.0694	1.36	----	----	---	190.3	5
^c B-57	.0689	1.35	90	66.7	7.3	191.1	20
^d B-56	.0734	1.43	32.5	22.7	6.4	191.4	20
B-52	.0675	1.32	----	----	---	191.5	10
B-50	.0779	1.52	53	34.9	6.5	191.5	15
^d B-58	.0696	1.36	27	19.9	6.5	191.6	22
^c B-55	.0751	1.47	113.5	77.2	7.0	191.8	20
B-53	.0680	1.33	57.5	43.2	6.3	191.9	20
B-54	.0697	1.36	56	41.2	6.3	193.3	30
B-46	.0688	1.34	51	38.1	5.8	193.5	15
^e B-47	.0713	1.39	0	----	---	194	---
B-45	.0713	1.39	60.5	43.5	5.8	194.3	15
B-41	.0687	1.34	58	43.3	2.5	197.3	7
B-44	.0659	1.29	64	49.6	4.5	197.8	15
B-42	.0723	1.41	85.5	60.6	3.8	201.3	10
B-43	.0780	1.52	114	75	3.0	206	10

^aInitiator added, azoisobutyronitrile 10^{-2} M.

^bNo intensifier.

^cIntensifier concentration, 2×10^{-3} M.

^dIntensifier concentration, 0.5×10^{-3} M.

^eNo oxygen (argon atmosphere).

^fNeat diphenylanthracene.

TABLE III.—WAVELENGTH
CHARACTERISTICS OF
VARIOUS BANDPASS
FILTERS

Color	Peak transmission, nm	Bandpass range, nm
Red	650	625 to 675
Green	525	500 to 550
Blue	425	400 to 475
Yellow	585	575 to 595

TABLE IV.—SUMMARY OF CHEMILUMINESCENCE DATA FOR
VARIOUS BANDPASS FILTERS

[Temperature, 187.1 to 187.3 °C; catalyst, aluminum alloy 2024.]

Test	Lubricant weight, g	Normalized weight	Maximum light emission, I_{\max} , arbitrary units	Normalized maximum light emission, I'_{\max}	Filter
Neat TMPTH					
B-75	0.1112	1.90	1.15	2.19	None
B-76	.1139	1.94	.66	1.28	Yellow
B-78	.1073	1.83	.13	.24	Green
B-79	.1097	1.87	.20	.28	Red
B-80	.0779	1.33	.38	.38	Blue
TMPTH with 10^{-3} M DPA					
B-87	0.0688	1.17	4.61	5.40	None
B-85	.0755	1.29	2.98	3.84	Yellow
B-84	.0658	1.12	.16	.18	Green
B-83	.0586	1.00	.15	.15	Red
B-82	.0612	1.05	2.63	2.76	Blue

1. Report No. NASA TP-2611		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Ester Oxidation on an Aluminum Surface Using Chemiluminescence				5. Report Date July 1986	
				6. Performing Organization Code 505-33-62	
7. Author(s) William R. Jones, Jr., Michael A. Meador, and Wilfredo Morales				8. Performing Organization Report No. E-2647	
				10. Work Unit No.	
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135				11. Contract or Grant No.	
				13. Type of Report and Period Covered Technical Paper	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546				14. Sponsoring Agency Code	
15. Supplementary Notes					
16. Abstract The oxidation characteristics of a pure ester (trimethylolpropane triheptanoate) were studied by using a chemiluminescence technique. Tests were run in a thin-film microoxidation apparatus with an aluminum-alloy catalyst. Conditions included a pure-oxygen atmosphere and a temperature range of 176 to 206 °C. Results indicated that oxidation of the ester (containing 10 ⁻³ M diphenylanthracene as an intensifier) was accompanied by emission of light. The maximum intensity of light emission I_{\max} was a function of the amount of ester, the concentration of intensifier, and the test temperature. The induction period, or the time to reach one-half of maximum intensity $t_{1/2}$, was inversely proportional to test temperature. Decreases in light emission at the later stages of a test were caused by depletion of the intensifier.					
17. Key Words (Suggested by Author(s)) Chemiluminescence Oxidation Ester			18. Distribution Statement Unclassified - unlimited STAR Category 27		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of pages 15	
				22. Price* A02	

*For sale by the National Technical Information Service, Springfield, Virginia 22161

NASA-Langley, 1986